

NRL Report 6270

Flammability Properties of Hydrocarbon Fuels

Part 1 - Interrelations of Flammability Properties of n-Alkanes in Air

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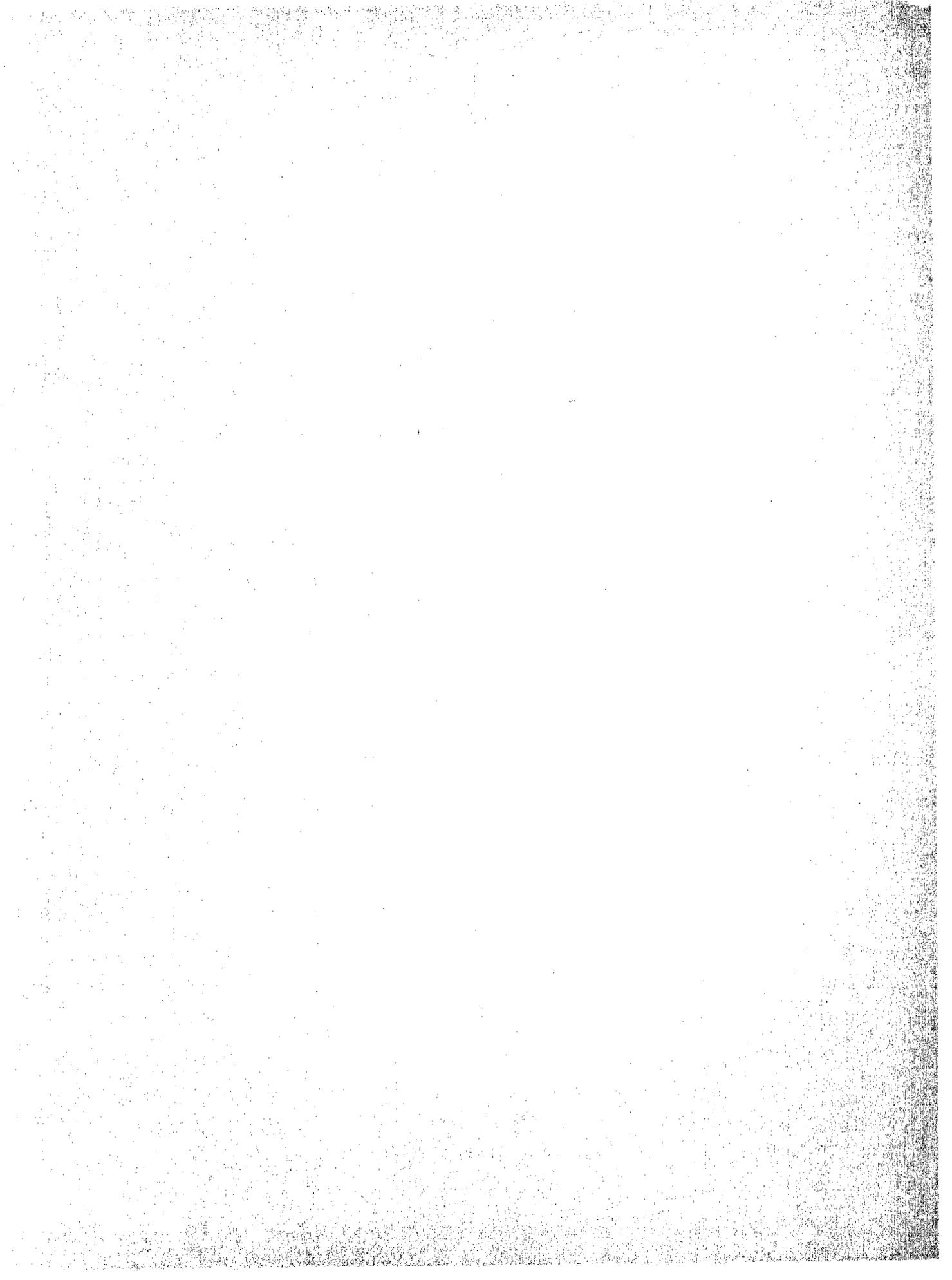
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ABSTRACT

By a systematic study of literature data, mathematical equations have been derived which describe the interrelationships of flammability and other related properties of the n-alkanes. The properties which have been correlated are: lower and upper flammability limits, flash point, vapor pressure (at the flash point), flammability index ("explosiveness"), boiling point, stoichiometric concentration, heat of combustion, molecular weight, and carbon number. Good agreement was found between average literature data and values calculated by the derived equations. From a given flammability property, by use of the derived equations, it is possible to predict the other properties, as well as the relative magnitudes of changes in these properties as a result of a change in the given property.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

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FLAMMABILITY PROPERTIES OF HYDROCARBON FUELS
PART 1 - INTERRELATIONS OF FLAMMABILITY PROPERTIES
OF n-ALKANES IN AIR

INTRODUCTION

Users of large quantities of flammable liquids and gases must be constantly alert against the dangers of fire and explosion in their storage, transportation, and use. Hydrocarbon fuels and similar petroleum derivatives, which are widely used on sea, ashore, and in the air, constitute a major portion of the flammable liquids and gases which are used throughout the world. Experience has shown that accidental fires and explosions which can occur in their handling may result in serious property damage, injury, and loss of life. For this reason, the flammability properties of hydrocarbon fuels are of considerable concern to the Navy, since understanding these properties helps make it possible to recognize and predict hazardous situations and to take proper steps to eliminate them.

Numerous flammability properties exist which may be measured experimentally, such as flash point, fire point, heat of combustion, flammability limits, spontaneous ignition temperature, explosiveness, ignition energy, and vapor pressure. Some of these properties may be determined with a fair degree of accuracy. Their limiting values are sometimes listed in specifications for the purchase and acceptance of fuels in order to keep the flammability hazard to a minimum. Aviation fuels, which are stored and handled on aircraft carriers at sea, require special fire-safety precautions and restrictions. JP-5 jet fuel, for example, which is used by the U.S. Navy for carrier-operated jet aircraft, must have a minimum flash point of 140°F and a maximum explosiveness of 50 percent to be acceptable (1).

Although the hydrocarbon and fuel literature is well stocked with flammability data, there is a great need for a clearer understanding of the meaning and significance of individual data and the quantitative relationships among them. It would be very useful to be able to predict the various flammability properties of a given fuel mixture either from its composition or from any one of its other flammability or related physical or chemical properties. Knowledge of the interrelations of the flammability properties of hydrocarbon fuels is useful in many ways. It can supply information for fuel evaluation in engine performance or fire-safety studies which is required for the writing of proper specifications and procedures for the purchase, safe handling, and efficient use of fuels. This knowledge can be helpful also in the elucidation of the fundamental processes of hydrocarbon oxidation, ignition, and combustion. In addition, it can be of assistance in data evaluation to detect experimental or other errors resulting from variations in method and technique, or from other sources.

Automotive and aviation gasolines, diesel and jet fuels, and similar petroleum distillate fractions consist chiefly of complex hydrocarbon mixtures which vary in composition (qualitatively and quantitatively) between different types of fuel and even vary between fuels which are of similar type. Flammability properties depend not only on the chemical composition of the fuel but also on other factors, which include temperature, pressure, and the composition of the surrounding atmosphere. The number of variables in a study of the interrelations of the flammability properties of hydrocarbon fuels is therefore very large, and it is evident that simplification is necessary to make any progress with this problem. This Laboratory has been especially interested in jet fuels for

many years. These fuels consist almost entirely of hydrocarbon mixtures of normal, branched chain, and cyclic paraffins and lesser amounts of aromatic and unsaturated hydrocarbons (2). Since paraffins and cycloparaffins are very similar in most of their properties and together make up 75 to 90 percent of most aircraft fuels (2), it was felt that a study of the n-alkanes, if fruitful, might be extended to other hydrocarbons and actual fuel mixtures, such as jet fuels in air and other atmospheres. Thus, the purpose of this preliminary study was to discover whether useful interrelationships of the flammability and related properties of the n-alkanes in air exist. It was decided to begin the work with a systematic study of available literature data.

EARLIER WORK

Correlations of the various flammability properties with each other and with other physical properties have been made by others for the n-alkanes, as well as for other hydrocarbons and for their mixtures. For example, Butler et al. (3) found a linear relationship between flash point and boiling point for distillate mixtures. Gwinn (4) found similar relationships for pure hydrocarbons. Spakowski (5) derived empirical relationships of lower and upper flammability limits with molecular weights and heats of combustion for pure hydrocarbons and fuels. Several workers (2,5-10) found a linear relationship between the net molar heat of combustion and the reciprocal of the lower flammability limit of pure hydrocarbons and fuel mixtures. Zabetakis et al. (11) reported that the lower flammability limit is a fairly constant value for a wide variety of paraffins and isoparaffins, and for a kerosene sample, when the concentration of hydrocarbon vapor at the lower flammability limit in air is expressed on a weight of hydrocarbon combustible to volume of air basis and reduced to standard conditions of temperature and pressure. The average concentration was 48 mg of combustible per liter of air at 26°C. A linear relationship between the vapor pressure at the flash point and the reciprocal of molecular weight was reported by Butler et al. (3) and Mullins (12,13) for mixtures of hydrocarbons and fuels, respectively. Mullins (12,13) also reported empirical equations relating flash points, vapor pressure, temperature, and lower flammability limits for fuel mixtures. An equation for calculating the flash point of a blend of lubricating oils from additive logarithmic functions of the flash points of the individual components was derived by Thiele (14).

The various equations for the interrelationships of the combustion and related properties of hydrocarbon mixtures and fuels which have been reported are limited in scope, and in most cases are only approximations. This is due chiefly to a general attempt to lump together the properties of many types of structurally different hydrocarbon compounds or their mixtures. This is an additional reason why it was decided to focus attention on a homologous series of pure compounds, such as the n-alkanes, in order to determine whether more exact interrelationships might be discovered which perhaps would be masked by a diversity of compounds in complex mixtures.

Because of its large structural dependence (15) as compared to other flammability properties, spontaneous ignition was not included at this time.

VARIATION WITH CARBON NUMBER

The orderly variation of the physical properties of the n-alkanes with molecular weight or carbon number has been well demonstrated and is applicable to the flammability properties as well (5). In general, this has been the basis of the technique which has been employed in the present work to derive the mathematical equations which describe the interrelationships of the properties of the n-alkanes. For each property, average literature data were plotted against carbon number, and equations were derived to describe these relationships. The constants of the equations were calculated from the data

by the method of least squares (16). The properties which were studied, along with their symbols and units and their derived equations, are shown in Table 1.

Table 1
Symbols, Units, and Derived Equations for Flammability and Related Properties of n-Alkanes in Air at Atmospheric Pressure

Property	Equation f(n)
(a) Carbon Number (n)	n
(b) Molecular Weight (\bar{M})	$\bar{M} = 14.027n + 2.0160$
(c) Boiling Point (t_B , °C)	$(t_B + 293.2)^2 = 21,580n$
(d) Net Molar Heat of Combustion (ΔH_m , kcal/mole)	$\Delta H_m = 146.91n + 47.496$
(e) Lower Flammability Limit at 25°C (L, %v/v)	$1/L = 0.1347n + 0.04353$
(f) Upper Flammability Limit at 25°C (U, %v/v)	$1/U = 0.01337n + 0.05151$
(g) Stoichiometric Concentration (C_s , %v/v)	$1/C_s = 0.07160n + 0.03387$
(h) Flash-Point Temperature (t_F , °C)	$(t_F + 277.3)^2 = 10,410n$
(i) Vapor Pressure at t_F (p_F , atm)	$1/p_F = 14.04n$
(j) Flammability Index at 125°F (E_i) $C_6 - C_{16}$; $E_i = C/L$, and C = actual fuel-vapor concentration (%v/v) at 125°F	$\log E_i = 3.966 - 0.383n$

In the case of molecular weight, which of course is a primary relationship and is not derived from literature data, \bar{M} itself is a direct linear function of n:

$$\bar{M} = 14.027n + 2.0160. \tag{1}$$

The equation for boiling point is

$$(t_B + 293.2)^2 = 21,580n. \tag{2}$$

The indirect expression $(t_B + 293.2)^2$ is a linear function of n. In the case of molar heat of combustion, the equation is

$$\Delta H_m = 146.91n + 47.496. \tag{3}$$

Equations (2) and (3) are plotted as straight line graphs in Fig. 1, and averaged literature data (17,18) are superimposed on the graphs for comparison. The data are also shown in Table 2. The agreement with the literature data is good for t_B and very good for ΔH_m .

Since Eqs. (1) through (3) are each functions of n, they may be treated as simultaneous equations. For example, the relationship of boiling point or heat of combustion to molecular weight, or to each other, may be readily obtained. The application of this technique to the various flammability and related properties of the n-alkanes will be described in the following section.

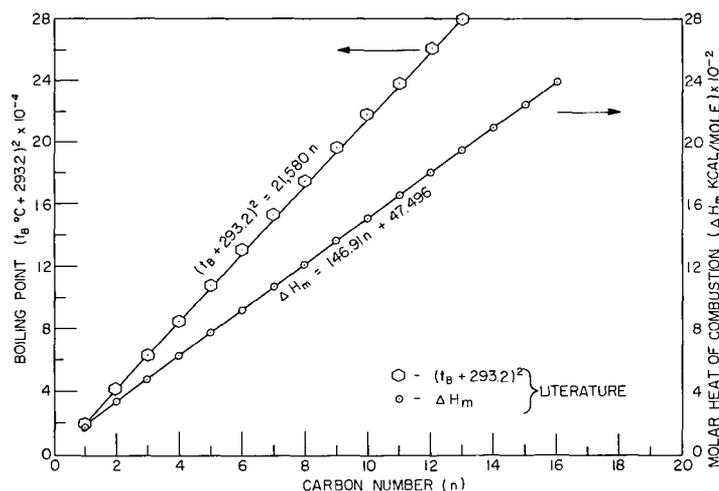


Fig. 1 - Boiling point and heat of combustion versus carbon number for n-alkanes

Table 2
Molecular Weights, Boiling Points, and
Heats of Combustion of n-Alkanes

Carbon No.	Molec. Wt.*	Boiling Point (t_B , °C)		Heat of Combust. (ΔH_m , kcal/mole)	
		Lit. (17)	Calc.†	Lit. (17,18)	Calc.‡
(n)	(\bar{M})				
1	16.043	-162	-146	191.76	194.41
2	30.070	-89	-86	341.26	341.32
3	44.097	-42	-39	488.53	488.24
4	58.124	-0.5	0.6	635.05	635.15
5	72.151	36	35	782.04	782.07
6	86.178	69	67	928.93	928.98
7	100.205	98	96	1075.85	1075.89
8	114.232	126	122	1222.77	1222.81
9	128.859	151	148	1369.70	1369.72
10	142.286	174	171	1516.63	1516.64
11	156.313	196	194	1663.55	1663.55
12	170.340	216	216	1810.48	1810.46
13	184.367	235	236	1957.40	1957.38
14	198.394	254	257	2104.32	2104.28
15	212.421	271	276	2251.24	2251.21
16	226.448	287	294	2398.17	2398.12

$$*\bar{M} = 14.027n + 2.016.$$

$$†(t_B + 293.2)^2 = 21,580n.$$

$$‡\Delta H_m = 146.91n + 47.496.$$

CHOICE AND HANDLING OF LITERATURE DATA

Since wide variations were often found in the literature data for specific properties of individual compounds, judicious choices were made. The basis of choice in general was rejecting data whose deviation was excessive using standard statistical techniques (16) and maintaining uniformity where necessary in the choice of experimental methods employed to obtain the data. Arithmetic means of the selected literature data were calculated. The method of least squares which was applied to the average literature data to calculate the constants of the mathematical equations thus served as a second averaging step.

As a general rule, methane did not fall in line with the other members of the n-alkane series, and it was found necessary in most cases in this work to omit it. Methane data were not used in the derivation of the various equations.

FLAMMABILITY LIMITS AND STOICHIOMETRIC CONCENTRATIONS

Flammability limits have been defined in rather precise terms (7). The experimental values for these limits, however, depend on the method and the nature of the apparatus employed, e.g., the direction of propagation. For consistency, literature flammability data used in this work are based on a vertical-tube apparatus for upward propagation, which is the technique most generally used (7). Limits in this work are expressed as percent by volume and are in air at room temperature.

Applying to the lower and upper flammability limits a technique similar to that employed with boiling point and heat of combustion, the following equations were derived:

$$1/L = 0.1347n + 0.04353 \quad (4)$$

$$1/U = 0.01337n + 0.05151 \quad (5)$$

$$1/C_s = 0.07160n + 0.03387 \quad (6)$$

The stoichiometric concentration C_s , which is included for comparison, assumes complete combustion to carbon dioxide and water.

Direct plots of U and L versus n , which illustrate the variation of flammability range, are shown in Fig. 2; and plots of the reciprocal functions (Eqs. (4) through (6)) are shown in Fig. 3. As before, the curves represent calculated values, and the points shown are averaged literature values.

In general, except for methane, there was good agreement between literature and calculated values for both lower and upper flammability limits as is also shown in Table 3. Agreement between calculated and averaged literature data is better for L than for U . The literature data for upper flammability limits were in relatively poor agreement among themselves and less available; therefore, the derived equation for U (Eq. (5)) may be less reliable.

It is now possible to derive our first flammability interrelationship. By simultaneous solution of the equations for molar heat of combustion and lower flammability limit (Eqs. (3) and (4)), we see that their product is constant,

$$L \Delta H_m = 1091 \quad (7)$$

This is in agreement with the findings of others (5-9). A plot of the reciprocal of L versus ΔH_m (Fig. 4) is linear and goes through the origin. It shows good agreement with average literature values with an average relative error of $\pm 2.1\%$.

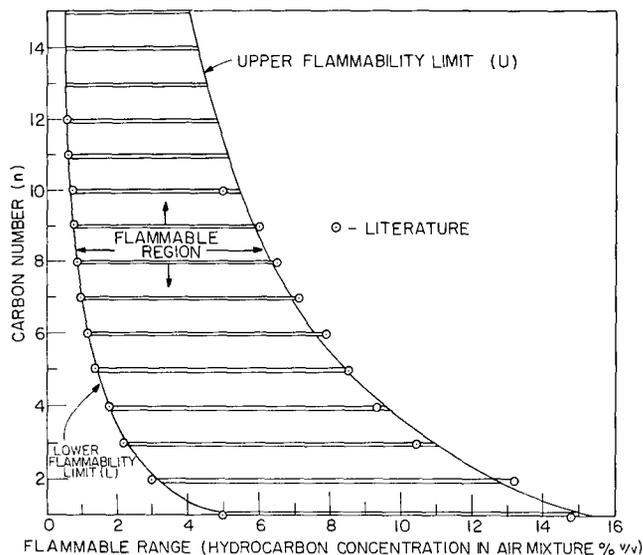


Fig. 2 - Flammability range versus carbon number for n-alkanes

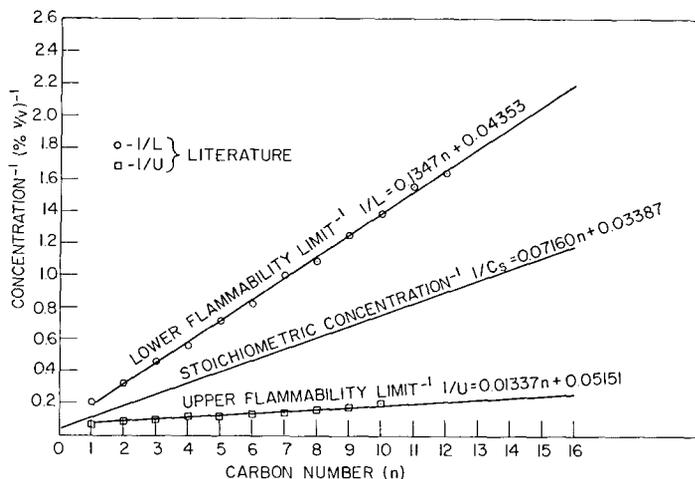


Fig. 3 - Flammability limits versus carbon number for n-alkanes

The next important interrelationship is that of the lower and upper flammability limits, which we obtain from Eqs. (4) and (5):

$$1/U = 0.0993(1/L) + 0.0472 \quad (8)$$

A plot of U versus L is shown in Fig. 5, and the reciprocal of L versus the reciprocal of U is shown in Fig. 6. Averaged literature data are in fair agreement with the calculated values.

Analogous flammability interrelationships may also be calculated for other combinations of these properties by use of the above equations.

Table 3
Flammability Limits of n-Alkanes

Carbon No. (n)	Lower Limit (L, %v/v)		Upper Limit (U, %v/v)	
	Lit. Av.*	Calculated†	Lit. Av.*	Calculated‡
1	5.0	5.6	14.8	15.4
2	3.0	3.2	13.2	12.8
3	2.2	2.2	10.4	10.9
4	1.8	1.7	9.3	9.5
5	1.4	1.4	8.4	8.4
6	1.2	1.2	7.8	7.6
7	1.0	1.0	7.1	6.9
8	0.92	0.89	6.5	6.3
9	0.80	0.80	6.0	5.8
10	0.72	0.72	5.0	5.4
11	0.64	0.66	-	5.0
12	0.61	0.60	-	4.7
13	-	0.56	-	4.4
14	-	0.52	-	4.2
15	-	0.48	-	4.0
16	-	0.46	-	3.8

*From Refs. 5, 7, 8, 10, 11, 19, 20.

† $1/L = 0.1347n + 0.04353$.

‡ $1/U = 0.01337n + 0.05151$.

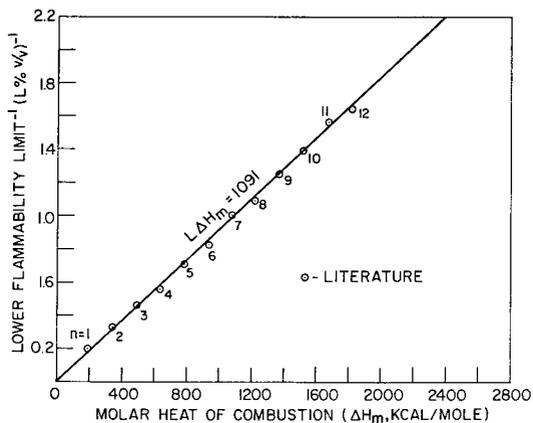


Fig. 4 - Lower flammability limit versus heat of combustion for n-alkanes

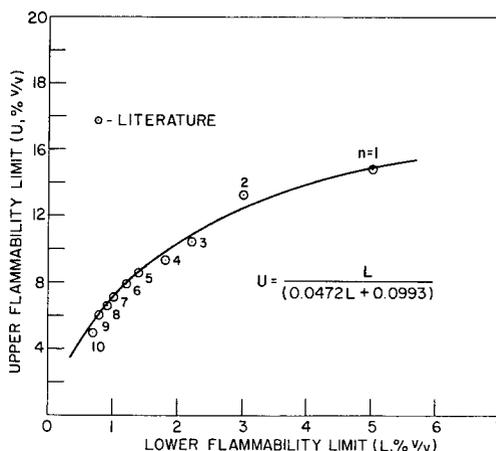


Fig. 5 - Upper versus lower flammability limits for n-alkanes

LOWER FLAMMABILITY LIMITS AND TEMPERATURE

Flammability limits do not vary significantly with moderate changes in temperature (7,22). However, when comparing data from wide ranges of temperature, the variations of flammability limits with temperature must also be taken into account. As pointed out by Coward and Jones (7), there is an inverse relationship between the lower flammability limit and temperature, so that the limit L_t decreases approximately linearly with temperature. Combining the findings of Zabetakis et al. (11) and White (22), an average

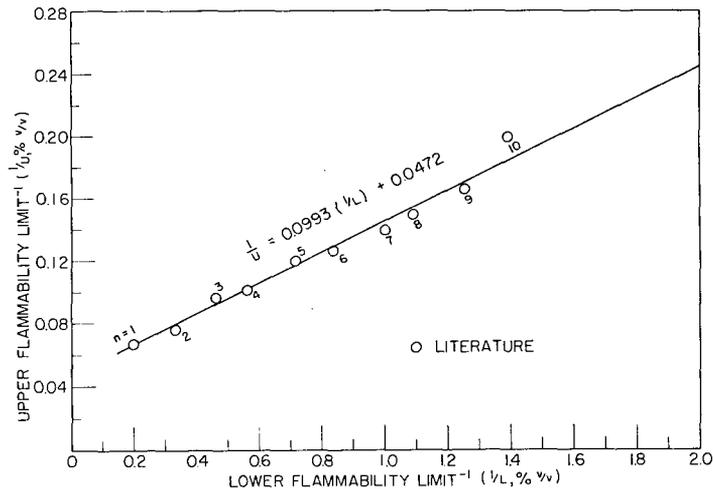


Fig. 6 - Upper versus lower flammability limits for n-alkanes (linear plot)

quantitative relationship between lower limit and temperature for the n-alkanes was derived which was used in certain of these calculations, as will be shown. The equation for the lower flammability limit L_t at a given temperature t °C as a function of the limit L at 25°C and of t is as follows:

$$L_t = 1.02L(1 - 7.75 \times 10^{-4} t) . \quad (9)$$

Thus, knowing the flammability limit at room temperature, or about 25°C (L), the limit at any temperature t can be calculated. The equation predicts an approximately 8% decrease in L_t with a temperature rise of 100°C. This equation is approximate and is based on average values for several hydrocarbons. However, since the temperature correction is small, it does not introduce a serious error in the calculations.

FLAMMABILITY LIMITS ON A WEIGHT-TO-VOLUME BASIS

Since it is sometimes customary to express flammability limits on a weight-to-volume basis, it was decided to examine the lower flammability limit equation (Eq. (4)) in that sense. If L_t is the lower flammability limit (volume basis) at a temperature t (as was discussed in the previous section), by applying the perfect gas law, we can derive the following equation for the lower flammability limit L_w (mg of fuel per liter of fuel-air mixture):

$$L_w = 121.87\bar{M}L_t/(t + 273.2) \quad (10)$$

where \bar{M} = molecular weight.

Equation (9) may be written

$$L_t = B_t L$$

where L is the flammability limit at 25°C (Table 1) and $B_t = 1.02(1 - 7.75 \times 10^{-4} t)$. Substituting for L_t (Eq. (9)) in Eq. (10),

$$L_w = 121.87B_t\bar{M}L/(t + 273.2) . \quad (11)$$

Table 4
Lower Flammability Limits of
n-Alkanes (mg/liter)

Carbon Number (n)	Lower Flammability Limit (L _w) at 25° (mg/liter)	
	Lit. Av.*	Calculated†
1	32.8	36.8
2	36.9	39.3
3	39.7	40.3
4	42.8	40.8
5	41.3	41.1
6	42.3	41.4
7	41.0	41.5
8	43.0	41.6
9	41.9	41.7
10	41.9	41.8
11	40.9	41.9
12	42.5	41.9
13	-	42.0
14	-	42.0
15	-	42.1
16	-	42.1
Infinity	-	42.6 = K _t

*From Refs. 5, 7, 8, 10, 11, 19, 20.

†L_w (25°C) = 42.6 (n + 0.1437) / (n + 0.3232).

If we now substitute the derived expressions for \bar{M} and L from Eqs. (1) and (4) respectively in Eq. (11), we get

$$L_w = 12,691B_t(n + 0.1437) / (n + 0.3232)(t + 273.2) \quad (12)$$

It is seen that L_w is a temperature dependent property, but at a given temperature it is a function of carbon number alone. If we let K_t equal the temperature correction factor term in Eq. (12), we get

$$L_w = K_t(n + 0.1437) / (n + 0.3232) \quad (13)$$

where K_t = 12,691B_t/T and is a constant factor at a given temperature.

The ratio of the two carbon number terms in Eq. (13) increases in magnitude as n increases, and (n + 0.1437)/(n + 0.3232) approaches unity as n approaches infinity. Thus L_w approaches K_t as its limiting value at n = infinity. For example, at 25°C, B_t = 1.000 and K₂₅ = 42.6. This is the limiting value of L_w (mg/l) at 25°C as n approaches infinity and is illustrated in Table 4 and Fig. 7. It can be seen that as n increases L_w rapidly assumes an approximately constant value above propane. The average literature values which are also shown agree fairly well with the calculated curve.

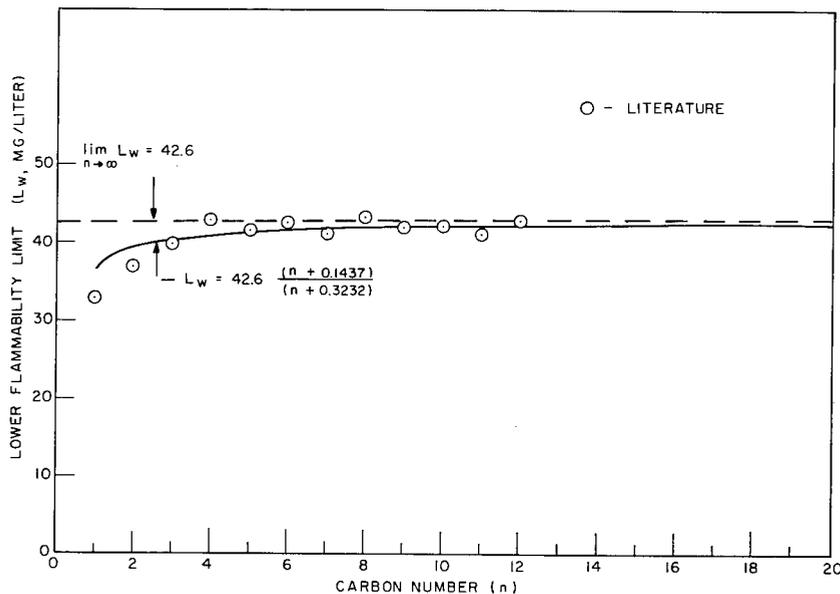


Fig. 7 - Lower flammability limit (mg/l) versus carbon number for n-alkanes

To illustrate the importance of temperature, a plot of K_t , the limiting value of L_w versus temperature is shown in Fig. 8. For example, at 0°C , $K_0 = 47.4$ mg/liter. This calculated value compares well with the average 48 mg combustible per liter of air reported by Zabetakis et al. (11) for series of 19 different hydrocarbons (from $n = 4$ to 12) and a kerosene sample, which were determined at 26°C and the results then reduced to 0°C . The "48 mg/liter of air" is not a concentration term in the usual sense but rather is a ratio of the weight of combustible to the volume of air in the fuel-air mixture. However, the slight discrepancy due to the two different modes of expressing concentration (47.4 mg/liter compared to 48 mg/liter of air) is small for hydrocarbons above propane, and the error rapidly becomes negligible as n increases, approaching zero as n approaches infinity.

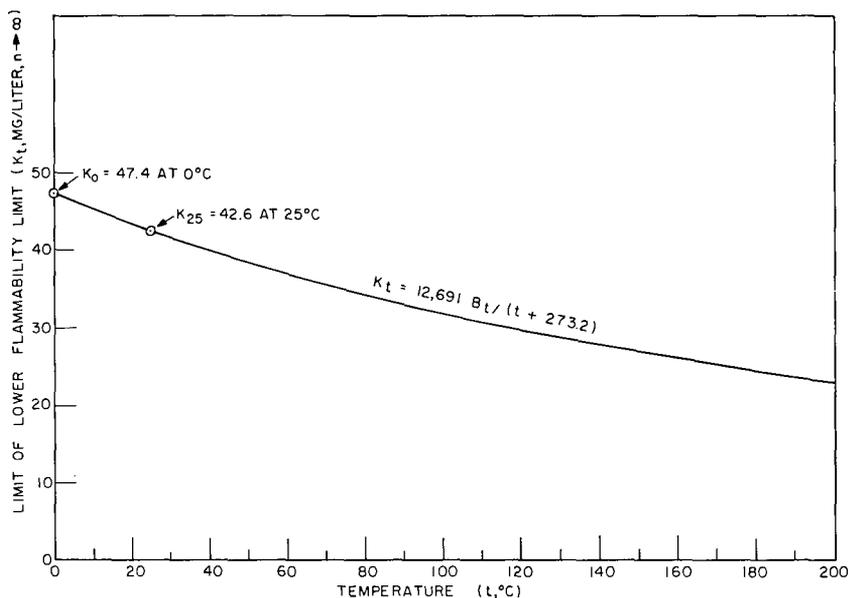


Fig. 8 - Limiting value of lower flammability limit (mg/l) versus temperature for n-alkanes ($n = \infty$)

There has been a tendency on the part of some workers in the combustion field to refer to this average constant value (48 mg at 0°C for example) without reference to temperature, thus leaving the impression that the value is an overall average constant for the lower flammability limit of hydrocarbons at all temperatures. Actually the "constant" is a function of temperature, which always should be specified.

FLASH POINT

Because of relatively poor agreement in the literature for flash-point data, instead of deriving the equations as previously from averaged literature data, a different approach was used. There are many definitions of flash point, most of them based on the experimental method of determining it, but a more fundamental definition which is sometimes used by workers in this field (21) defines flash point as "the minimum temperature at which sufficient vapor is released by a liquid or solid to form a flammable vapor-air mixture at one atmosphere pressure." In other words, flash point is that temperature at which the vapor pressure of the fuel (in atmospheres) is equivalent to the concentration at the lower flammability limit (mole fraction or its equivalent, $L \%v/v \times 10^{-2}$). Thus,

within this meaning, the intersection of the vapor pressure and the lower flammability limit curves, both plotted against temperature, should be the temperature at the flash point. It was decided to investigate this technique. A theoretical plot, similar to a diagram by Van Dolah et al. (21), which demonstrates this concept is shown in Fig. 9. The flammable and non-flammable zones are indicated. The vapor pressure-temperature curve intersects the lower flammability limit-temperature curve at point A. The analogous intersection of the upper flammability limit-temperature and vapor pressure-temperature curves is shown at point B. Though this point is of interest, it will not be covered here. The flash point (t_F) and the corresponding vapor pressure (p_F) are indicated by temperature and pressure coordinates at the intersection A.

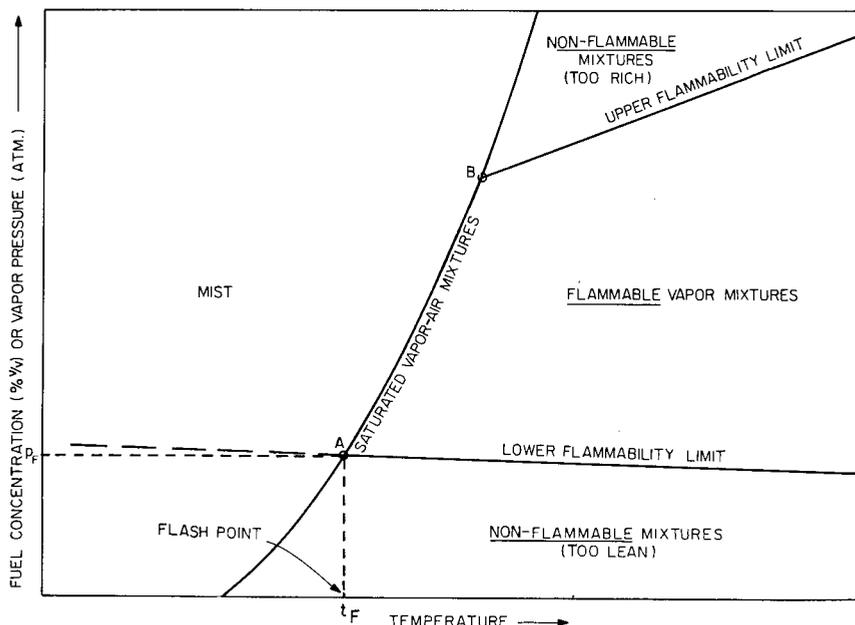


Fig. 9 - Vapor pressure and flammability limits versus temperature for a typical hydrocarbon fuel-air mixture

Actual pairs of curves were plotted for each of the n-alkanes up to a carbon number of 15 for both vapor pressure and lower flammability limit against temperature. The pairs of curves for the n-alkanes from $n = 5$ to 13 are shown in Fig. 10. The vapor pressure-temperature data were obtained from the literature (17,23). The lower flammability limit curves were obtained from calculated values of L and L_c from Eqs. (4) and (9). The points of intersection of all the pairs of curves for the 15 n-alkanes are shown as small circles in Fig. 11 along with averaged literature flash-point values (large crossed circles) superimposed on a plot of calculated p_F versus t_F values from the equation:

$$(t_F + 277.3)^2 p_F = 741.7 \tag{14}$$

Equation (14) was derived by least squares treatment of the points of intersection of the graphs.

In a similar manner, using the t_F and p_F values obtained from the graphs rather than averaged literature data, but using the same technique as employed for Eqs. (2) to

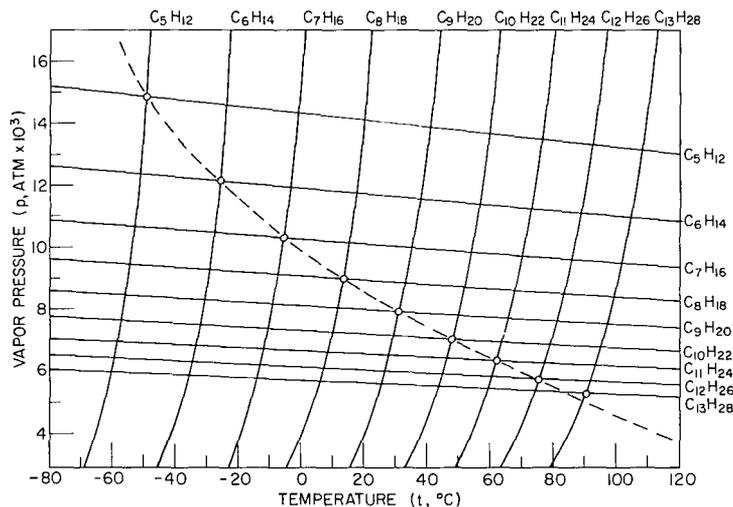


Fig. 10 - Vapor pressure and lower flammability limit versus temperature for n-alkanes

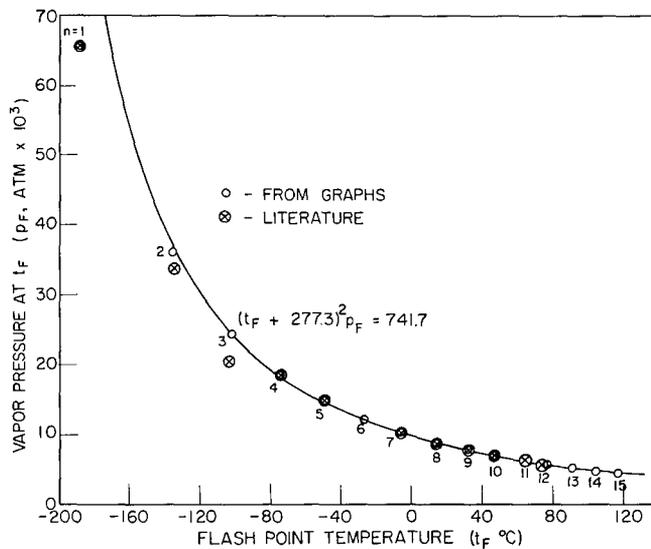


Fig. 11 - Vapor pressure at the flash point versus flash point for n-alkanes

(6), the following two equations were derived which give t_F and p_F as functions of n :

$$(t_F + 277.3)^2 = 10,410n \quad (15)$$

$$1/p_F = 14.04n \quad (16)$$

Plots of these equations are given in Fig. 12.

A comparison of averaged literature data with values derived both from the graphs and by calculation (Eqs. (15) and (16)) is given in Table 5. Examination of the data in Figs. 11 and 12 and Table 5 shows rather good agreement for flash-point data and fair

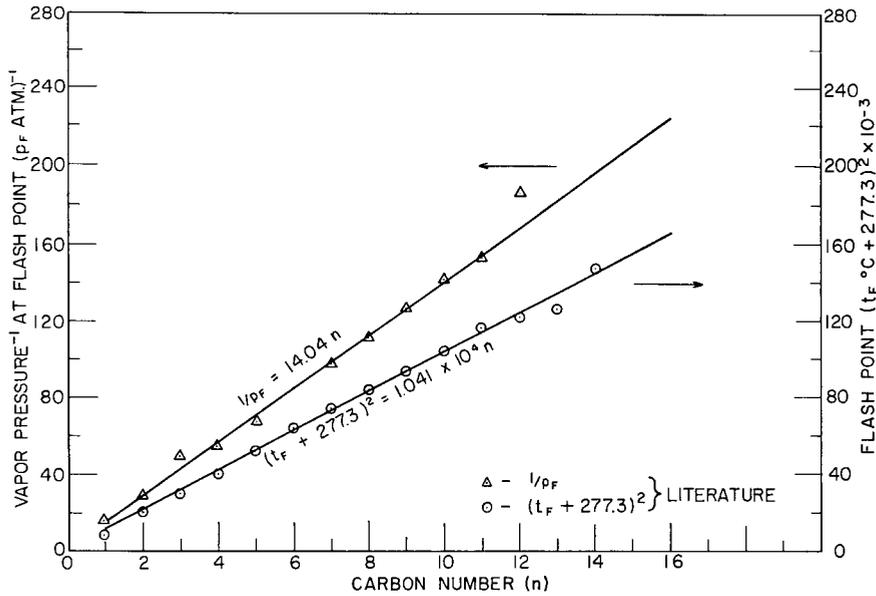


Fig. 12 - Vapor pressure at the flash point and flash point versus carbon number for n-alkanes

Table 5
Vapor Pressures at Flash Point and Molecular Weights of n-Alkanes

Carbon No. (n)	Recip. Molec. Wt. (1/M) × 10 ³	Vapor Pressure (p _F , atm × 10 ³ at t _F)			Flash Point (t _F , °C)		
		Lit. Av.*	Graph†	Calculated‡	Lit. Av.§	Graph†	Calculated¶
1	62.3	65.8**	65.8	71.2	-188**	-188	-175
2	33.3	33.5**	36.0	35.6	-135**	-135	-133
3	22.7	20.5**	24.5	23.7	-104**	-102	-101
4	17.2	18.5	18.5	17.8	-74	-74	-73
5	13.9	14.9	14.9	13.9	-49	-49	-49
6	11.6	15.1††	12.2	11.9	-23	-26	-28
7	10.0	10.3	10.3	10.2	-3	-6	-7
8	8.8	9.0	9.0	8.9	14	13	11
9	7.8	7.9	7.9	7.9	31	31	29
10	7.0	7.0	7.1	7.1	46	47	45
11	6.4	6.5	6.4	6.5	64	62	61
12	5.9	5.4	5.8	5.9	74	76	76
13	5.4	3.0**††	5.3	5.5	79**	90	91
14	5.0	6.0††	4.9	5.1	107	103	104
15	4.7	-	4.5	4.8	-	114	118
16	4.4	-	-	4.5	-	-	131

*p_F derived from literature average flash points and literature vapor pressure data (17, 23).

†From intersection of vapor pressure and lower flammability limit curves (Fig. 10).

‡1/p_F = 14.04n.

§From Refs. 3, 4, 17, 19, 20, 24.

¶(t_F + 277.3)² = 1.041 × 10⁴n.

**Only one or two values found in literature.

††Derived literature values of p_F for n-hexane and tri- and tetradecane appear to be in error. See text.

agreement for vapor pressure at the flash point, except for methane. The relatively poor agreement for p_F in certain cases, particularly for n-hexane and tri- and tetradecane, appears to be the result of discrepancies in the literature flash-point data for these hydrocarbons. The literature flash-point temperatures of -23 , 79 , and 107°C respectively for these three compounds, as shown in Table 5, are apparently out of line with the other n-alkanes; and this suggests a need to recheck these experimental values. Because of the logarithmic relationship between vapor pressure and temperature (17,23), small errors in t_F result in relatively large errors in p_F . The derived literature p_F values for n-hexane and tri- and tetradecane, 0.015 , 0.003 , and 0.006 atm respectively, are obviously in serious error and have not been included in the graphs (Figs. 11 through 13).

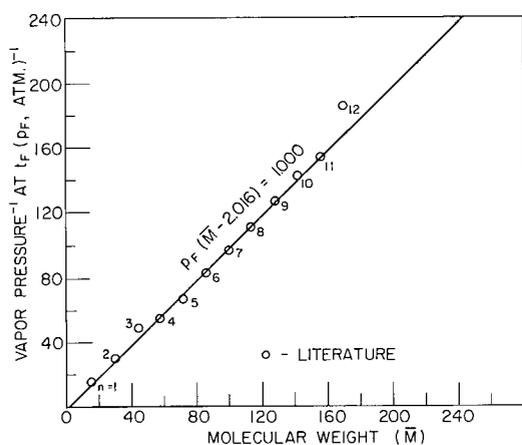


Fig. 13 - Vapor pressure at the flash point versus molecular weight for n-alkanes

From Eqs. (15) and (16) and the previously derived equations, interrelationships of the flash-point properties, t_F and p_F , and other properties may be derived. For example, the interesting relationship between vapor pressure at the flash point and molecular weight may be derived from Eqs. (1) and (16):

$$p_F (\bar{M} - 2.016) = 1.000 \quad (17)$$

This relationship is plotted in Fig. 13 along with literature data. The reciprocal molecular weight data in Table 5 are also presented to illustrate this relationship. This relationship is in accord with the results of Mullins (12,13) for fuel mixtures.

The relationship between flash point and boiling point may be derived from Eqs. (2) and (15):

$$t_F = 0.6946 t_B - 73.7 \quad (18)$$

This relationship is plotted in Fig. 14, which also includes literature data. Equation (18)

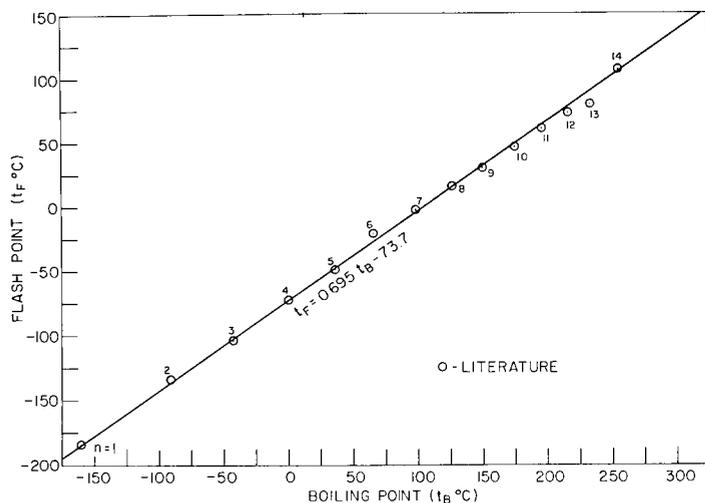


Fig. 14 - Flash point versus boiling point for n-alkanes

is in good agreement with that derived by Butler et al. (3) for a wide variety of hydrocarbon compounds where the slope and intercept are 0.683 and -71.7 (changed to centigrade), respectively.

The very important relationship between flash point and lower flammability limit may be derived from Eqs. (4) and (15):

$$(t_F + 277.3)^2 = 77,291(1/L) - 3365 \tag{19}$$

This relationship is plotted in Figs. 15 and 16, and literature data is included for comparison.

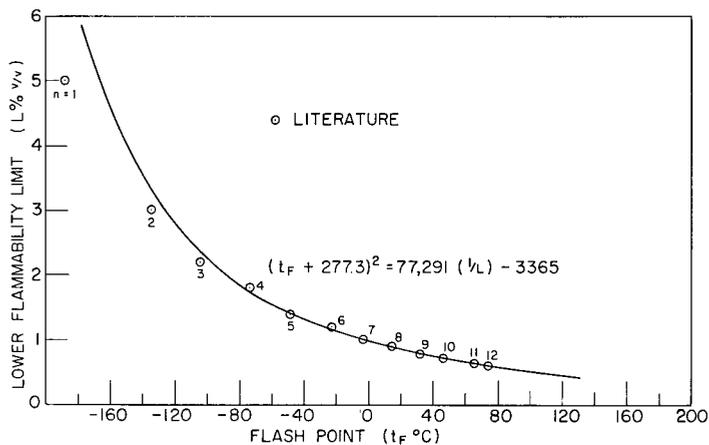


Fig. 15 - Flash point versus lower flammability limit for n-alkanes

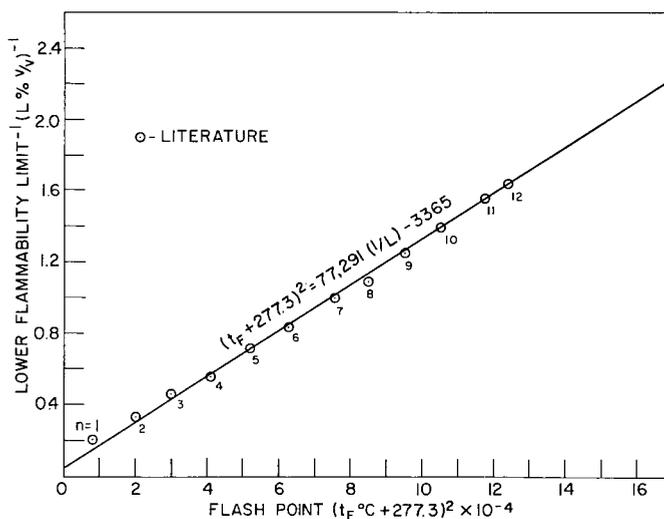


Fig. 16 - Flash point versus lower flammability limit (linear plot) for n-alkanes

FLAMMABILITY INDEX

Another useful flammability property, which can be measured readily for a given fuel vapor-air mixture, has been variously referred to as "percent explosiveness" (1,25) "explosivity" (26), or "percent of the lower explosive limit" (8). This property, which is temperature dependent, is actually a measure of potential flammability hazard rather than "explosiveness" as such. For this reason, the term "flammability index" is suggested as a more meaningful expression to describe this property and will be used in this report. All of these expressions, however, involve a common concept of the fraction or ratio of the actual concentration of fuel vapor to that at its lower flammability limit. The fraction may be expressed as a decimal or percentage of volume concentrations; but the former, which is based on unity rather than 100, is simpler and more direct and will be used as a basis of flammability units. If C_t is the volume concentration of fuel vapor at a given temperature t and if L_t is the lower flammability limit (%v/v), then the flammability index E_t is defined

$$E_t = C_t/L_t . \quad (20)$$

Thus, if the fuel vapor concentration in a given air-fuel mixture is equal to the concentration at the lower flammability limit ($C_t = L_t$), the flammability index is unity ($E_t = 1$). If E_t is greater than or equal to unity, the mixture is flammable and if E_t is less than unity, nonflammable.

The application of the flammability index concept to a mixture is not as simple as its application to a pure compound. The concentration of fuel vapor in the air over a liquid at atmospheric pressure will depend on its vapor pressure at any given temperature, the volume of the space over the liquid fuel, and the time allowed for evaporation.

By standard test methods (25), the flammability index is determined at 125°F (51.7°C) in a prescribed apparatus under conditions approaching equilibrium and using a standard fuel-air mixture at room temperature (assumed to be approximately 25°C) for a reference. For the pure n-alkanes, if we substitute vapor pressure at 125°F (in atmospheres) for its equivalent in volume percent concentration and L for L_t at 25°C in Eq. (20), the flammability index E_i at 125°F is

$$E_i = 100p_i/L . \quad (21)$$

From literature vapor pressure data (17,23) and calculated lower flammability limits (Eq. (4)), E_i was calculated for the n-alkane series from $n = 6$ to 16 using Eq. (21). Applying the same technique as was used previously for the other flammability properties, the following equation of E_i as a function of n was derived ($n = 6$ to 16):

$$\log E_i = 3.966 - 0.383n . \quad (22)$$

A graph of E_i versus n is shown in Fig. 17. Literature derived values based on average literature values for L (Table 3) are also shown. The linear relationship holds rather well in the range of n-alkanes shown. The n-alkanes below hexane were omitted because their vapor pressures at 51.7°C exceeded one atmosphere.

From Eq. (22) and the other flammability property equations (Table 1), relations between E_i and the other properties may be derived. Two important interrelations of E_i and L and of E_i and t_F were derived from Eq. (22) and Eqs. (4) and (15) respectively:

$$\log E_i = 4.090 - 2.843 (1/L) \quad (23)$$

$$\log E_i = 3.966 - 3.679 \times 10^{-5} (t_F + 277.3)^2 . \quad (24)$$

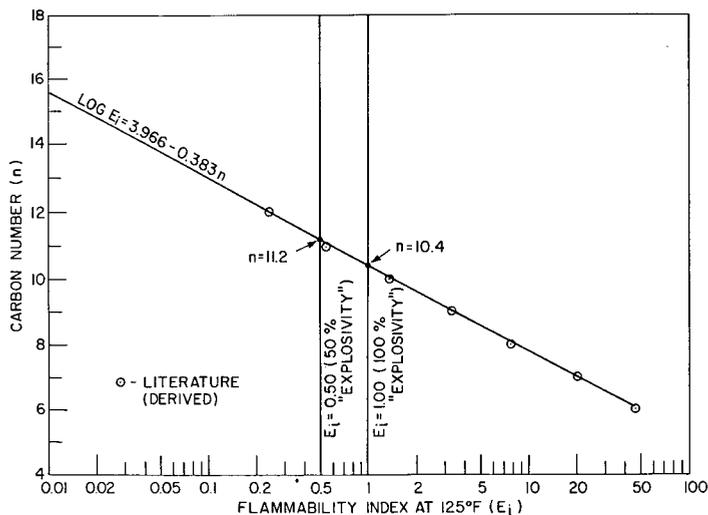


Fig. 17 - Flammability index versus carbon number for n-alkanes (n = 6 to 16)

Graphs of Eqs. (23) and (24) along with derived literature data are shown in Figs. 18 and 19.

AN APPLICATION TO A NAVY PROBLEM

As was mentioned in the introduction, the current military specification for JP-5 jet fuel (1) requires that JP-5 have a minimum flash point of 140°F and a maximum flammability index of 0.50 (50% explosiveness). In order to increase the available supply of this fuel, it has been proposed that the flash-point specification requirement be reduced from 140°F (60.0°C) to 130°F (54.4°C), if this would be feasible from the point of view of fire and explosion hazards in the storage and handling of this fuel both on ships and ashore. No change in the flammability index requirement of 0.50 or less has been suggested. Aside from the deeper questions of flammability and safety which are involved in such a change of flash-point specification, an immediate question to be answered is whether a fuel with a flash point of 130°F will meet the flammability index (explosiveness) requirement. It was interesting to apply the derived equations to this question. If we assume that JP-5 is a mixture of hydrocarbons consisting chiefly of the n-alkanes (2) and that the remaining hydrocarbons will not significantly deviate from the derived equations, we may then predict the effect on flammability index of a change in flash point. It is also possible to study in this way the effect of a change in any given flammability property on the others. "Critical" values for the more important flammability properties have been calculated for fuels having the present and proposed specification limits, and also for a flammable mixture chosen for reference; the results are shown in Table 6. Certain of these critical values are also indicated in Figs. 17 and 18, and the key relationships connected with the JP-5 specification problem are shown in Fig. 19. The following is an approximate equation which indicates how flammability index is affected by a change in flash point:

$$\% (\Delta E_i / E_i) / \Delta t_F = -3.8\% E_i / ^\circ F = -6.7\% E_i / ^\circ C . \tag{25}$$

Equation (25) was derived by taking the first derivative of log E_i with respect to t_F in Eq. (24), and using the delta or differential symbol to represent the changes in one variable as a result of a change in the other.

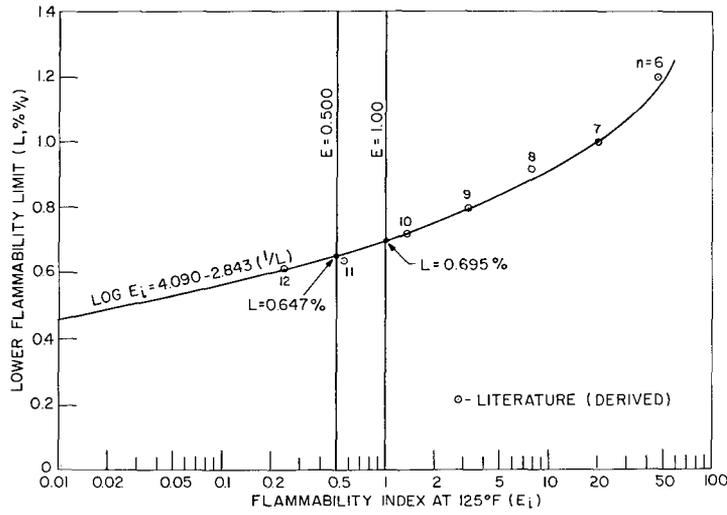


Fig. 18 - Flammability index versus lower flammability limit for n-alkanes ($n = 6$ to 16)

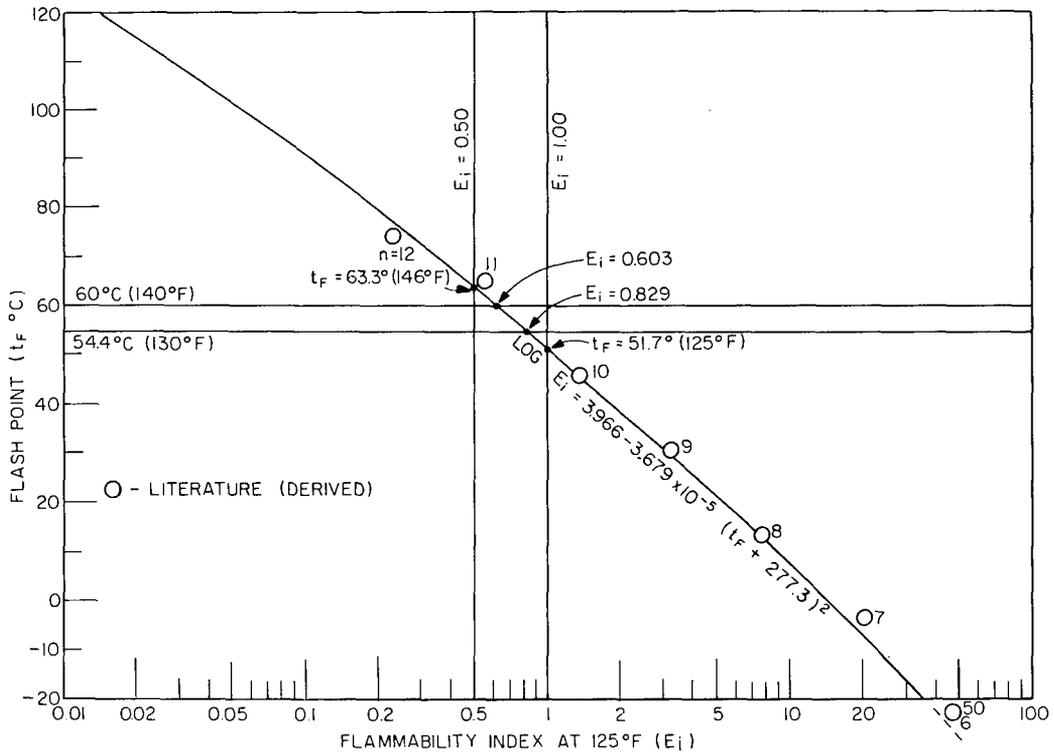


Fig. 19 - Flammability limit versus flash point for n-alkanes ($n = 6$ to 16)

Table 6
Calculated Critical Values at Specification Limits for n-Alkanes

Property	Flammable Mixture ($E_i = 1.0$)	Proposed Spec. ($t_F = 130^\circ\text{F}$, min.)	Present Specification	
			$t_F = 140^\circ\text{F}$, min.	$E_i = 0.50$, max.
Flammability index at 125°F (E_i) (max.)	1.00	0.83	0.60	0.50
Flash point (t_F $^\circ\text{C}$) (min.)	51.7	54.4	60.0	63.3
Flash point (t_F $^\circ\text{F}$) (min.)	125	130	140	146
Lower flammability ($L = \%v/v$)	0.70	0.68	0.66	0.65
Upper flammability ($U = \%v/v$)	5.25	5.19	5.06	4.98
Number of carbon atoms/molecule (n)	10.4	10.6	10.9	11.2
Molecular weight (\bar{M})	148	150	155	159
Boiling point (t_B , $^\circ\text{C}$)	180	184	193	198
Vapor pressure at 125°F (p_i , atm $\times 10^3$)	6.86	5.71	4.02	3.19
Molar heat of combustion (ΔH_m , kcal/mole)	1570	1600	1650	1690

In connection with the JP-5 specification problem, it can be seen from Eq. (25) that a 10°F (5.6°C) drop in flash point will cause an approximately 38% relative rise in flammability index.

From Table 6 and Fig. 19 it can be seen that a n-alkane with a flash point of 140°F (present specification) will have a flammability index of 0.60 (which is somewhat too high according to the specification), but a flash point of 130°F will result in a flammability index of 0.83 (which is excessively high).

AN APPLICATION TO A LABORATORY PROBLEM

In connection with the above problem, a question is raised which, although beyond the scope of this report, should at least be answered, even if only briefly. Further, this question demonstrates another use to which these derived equations may be put. The question is: Why do JP-5 jet fuels of 140°F flash point meet the 0.50 flammability index requirement if the equation (Eq. (24)) predicts that it should not ($E_i = 0.60$)?

The answer to this question involves the method of determining flammability index (25), the accuracy of which has long been suspect. Although there are other reasons, the chief factor is that the determination is made at 125°F , but the tubing through which the fuel vapors are channeled to the instrument are at room temperature. Since vapor pressure is an exponential function of temperature, the effect of this temperature drop is considerable and can result in condensation of vapors on the inner walls of the tubing, thus yielding an apparent lower flammability index value. The effect of ambient temperature on vapor pressure (17,23) and on E_i is shown in Fig. 20 for n-decane, which is given as an example. From the curve it can be seen that n-decane has a flammability index of 1.30 at 125°F which should not meet the specification; but at 95°F (a rather warm room temperature), for example, $E_i = 0.50$, which passes the test. These findings are in

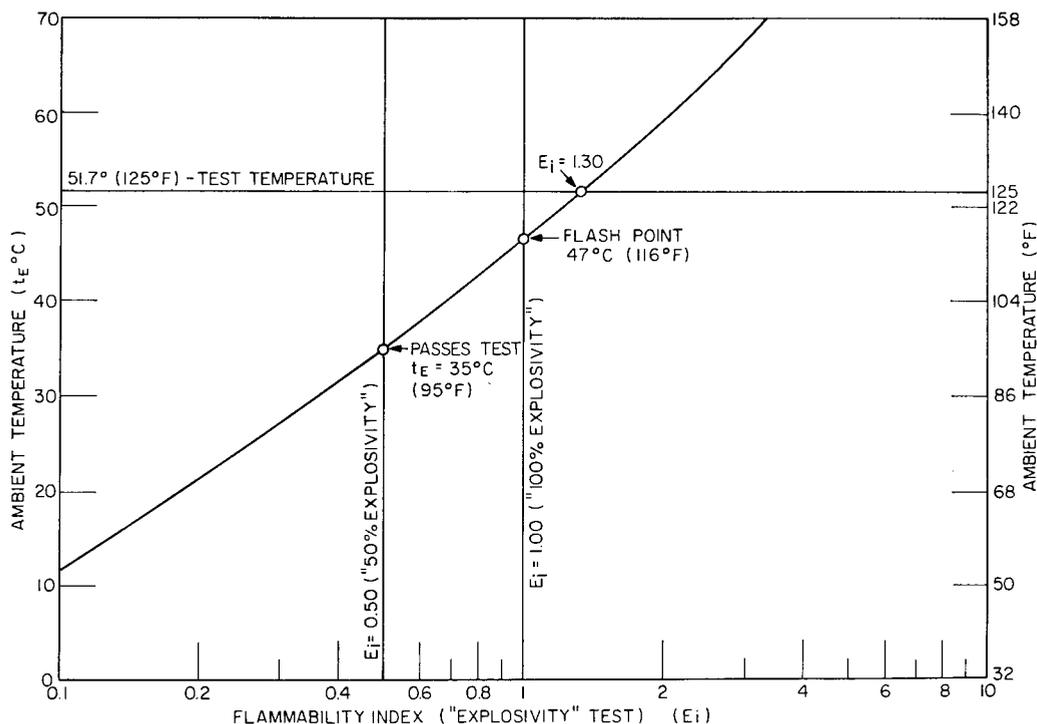


Fig. 20 - Flammability index test versus ambient temperature for n-decane

accord with unpublished work at this laboratory (26) for determining E_i of fuel vapors in air by charcoal absorption, where it was found that the standard test method for determining flammability index gave results which were approximately one half of the concentrations found by charcoal absorption.

For these reasons, it is recommended that the validity and accuracy of the explosivity test method be investigated. The present test method should be revised, if possible, in order to eliminate the above-mentioned discrepancies; or if necessary, an entirely new method should be developed.

SUMMARY

A technique has been developed by which it is possible to derive equations which describe interrelationships for flammability and related properties of the pure n-alkane hydrocarbons. The agreement of averaged literature data and calculated properties is good, except for methane. Although a detailed study of other hydrocarbon compounds and/or their mixtures has not been made as yet, it may be possible that equations of the type which have been derived, perhaps with different constants, may be applicable to these other hydrocarbons, and possibly also to certain non-hydrocarbon compounds and to mixtures.

It should be possible by means of these and similar equations to obtain additional fundamental and practical knowledge concerning the flammability properties of combustibles and concerning the experimental methods for their measurement.

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13. ABSTRACT <p>By a systematic study of literature data, mathematical equations have been derived which describe the interrelationships of flammability and other related properties of the n-alkanes. The properties which have been correlated are: lower and upper flammability limits, flash point, vapor pressure (at the flash point), flammability index ("explosiveness"), boiling point, stoichiometric concentration, heat of combustion, molecular weight, and carbon number. Good agreement was found between average literature data and values calculated by the derived equations. From a given flammability property, by use of the derived equations, it is possible to predict the other properties, as well as the relative magnitudes of changes in these properties as a result of a change in the given property.</p>			

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